



Short communication

Formic acid electrooxidation over carbon-supported nanoparticles of non-stoichiometric palladium carbide

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H I G H L I G H T S

- ▶ Pd–C interstitial solid solutions as catalysts for HCOOH electrooxidation.
- ▶ Any Pd/C can be easily transformed to PdC_x/C catalyst for HCOOH electrooxidation.
- ▶ PdC_{0.14}/C is more active and stable than Pd/C during HCOOH electrooxidation.

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Catalytic performance of the 5 wt.% Pd/C and 5 wt.% PdC_{0.14}/C catalysts for formic acid electrooxidation was compared under potentiodynamic (0.06–1.0 V vs. RHE, sweep rate 50 mV s^{−1}) and potentiostatic (0.2 and 0.3 V vs. RHE) regimes in 0.5 M HCOOH + 0.1 M H₂SO₄ solution at 25 °C. The non-stoichiometric palladium carbide catalyst demonstrates superior catalytic performance and stability during HCOOH electrooxidation as compared to the unmodified Pd/C precursor. The observed phenomenon is explained in terms of modification of electronic and adsorption properties of palladium caused by the embedding of carbon atoms in the interstitial sites of the crystalline lattice of Pd nanoparticles.

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1. Introduction

Being recognized as a promising portable power sources, direct formic acid fuel cells (DFAFC) have been addressed a great investigative effort during the last decade [1]. Apart from the problem of the sluggish kinetics of the oxygen reduction reaction on the cathode [2], which is common for all low-temperature fuel cells, further advancement of the DFAFC technology demands the development of the efficient anode catalyst for the HCOOH electrooxidation. From the points of view of both activity and stability, the palladium-based catalytic systems are advocated as the best option for the DFAFC anode [1]. The performance of palladium for the formic acid electrooxidation can be improved by combining Pd with a variety of metals, e.g. with Pt [3], Ru [4], Au [5], Ag [6], Bi [7], Pb [8], Sn [9], or with metalloids As [9] and B [10]. Occasionally, the enhanced activity of the modified palladium catalysts is rationalized in terms of a downshift of the *d*-band center of palladium

under the action of the promoter and resulting weakening of the adsorption of the poisoning intermediate of the HCOOH oxidation, which is formed when the reaction passes through the so-called ‘indirect’ route [3,10,11]. The exact chemical nature of the poisoning intermediate occurring on the surface of palladium catalysts during the electrooxidation of formic acid is still under debate. A recent *in situ* surface-enhanced infrared absorption spectroscopy study [12] suggests that the poisoning intermediate arising on the Pd surface is not carbon monoxide, as opposed to the platinum catalysts [13]. Notwithstanding this uncertainty, Yu and Pickup [14] fairly suggested that the principal reason of deactivation of Pd catalysts during the HCOOH electrooxidation is the formation of poisoning species from formic acid, rather than adsorption of OH, anions or impurities contained in the HCOOH fuel (which, undoubtedly, deactivate catalysts to a certain extent as well).

We have found recently that the incorporation of carbon atoms into the interstitial sites of the Pd crystalline lattice with the formation of non-stoichiometric palladium carbides has a strong promoting effect on the catalytic activity in the hydrogen electrode reactions and, most importantly, on the CO tolerance of palladium

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[15]. As demonstrated earlier in numerous theoretical and experimental studies (see [16,17] and references therein), the formation of the Pd–C solid solutions provokes substantial changes in the electronic state and adsorption properties of palladium with respect to various reagents. Indeed, this inevitably makes the (electro)catalytic properties of PdC_x notably different from those of unmodified Pd metal. These findings impelled us to study, for the first time, the catalytic performance of the carbon-supported nanoparticles of non-stoichiometric Pd carbides for the electro-oxidation of formic acid. A PdC_{0.14}/C catalyst described here was prepared by decomposition of ethylene over an unmodified Pd/C sample, which was also employed as a reference for the electro-catalytic tests.

2. Experimental

2.1. Materials

Palladium(II) chloride (PdCl₂, 59.9 wt.% Pd) was purchased from Voikov Chemical Plant (Moscow, Russia). H₂PdCl₄ was obtained by dissolution of PdCl₂ in concentrated HCl. Other reagents were of extra pure or analytical grade and used as purchased without further purification. For the catalyst preparation and electro-chemical measurements, high-purity gases (Ar 99.998%; N₂ 99.80%; H₂ 99.999%; CO 99.999%; C₂H₄ 99.99%) were used. Proprietary mesoporous graphite-like carbon material of the Sibunit family (sample Sib.15N with $S_{\text{BET}} = 15.6 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.074 \text{ cm}^3 \text{ g}^{-1}$, $V_{\mu} < 0.001 \text{ cm}^3 \text{ g}^{-1}$, $D_p = 11.4 \text{ nm}$) prepared in the Institute of Hydrocarbons Processing (Omsk, Russia) [18] was used as a catalyst support.

2.2. Preparation of the Pd/C and PdC_{0.14}/C catalysts

The Pd/C catalyst with 5 wt.% palladium loading was prepared using the precipitation technique, while the PdC_{0.14}/C catalyst was prepared by heating the parent Pd/C sample under C₂H₄ flow during 2 h at 300 °C following the procedures minutely described earlier in Ref. [15].

2.3. Characterization

X-ray diffraction (XRD) patterns of the support and catalysts were recorded on an HZG-4C diffractometer using CuK_α radiation ($\lambda = 0.15418 \text{ nm}$) and graphite monochromator. The data were collected for 10 s per step with a 0.05° step size in the 2θ range between 15° and 90°. The lattice constants of the Pd and PdC_{0.14} phases were determined from the positions of the corresponding (220), (311) and (222) diffraction peaks with the use of the least-squares refinement implemented by the POLYCRYSTAL program [19].

Transition electron microscopy (TEM) studies were carried out on a JEOL JEM-2010 electron microscope with a lattice resolution of 0.14 nm at a 200 kV accelerating voltage. At least 500 particles in the TEM images taken with a medium magnification were considered for the calculation of the mean linear ($d_l = \Sigma d_i/N$) diameters of Pd-containing particles.

2.4. Electrochemical measurements

Electrochemical measurements were performed with an Autolab PGSTAT 30 potentiostat equipped with a Scangen module in a three-electrode cell comprised of individual compartments for each electrode. The counter electrode (high surface area Pt foil) and the reference electrode (mercury/mercury sulfate) compartments were connected to the working electrode compartment through

a glass frit and a Luggin capillary, respectively. During the measurements, the whole cell was thermostated at 25 °C. All electrode potentials reported in this paper are referred to the reversible hydrogen electrode (RHE).

A glassy carbon (GC) cylinder (Ø5 mm) was used as a substrate for the working electrodes, which were prepared following the procedure described in Ref. [15]. The loading of Pd on the electrode surface was typically in the range of 2–4 $\mu\text{g cm}^{-2}$ (geom.). The contact with the deaerated supporting electrolyte was established at a controlled potential of 0.4 V vs. RHE. For CO-stripping experiments, carbon monoxide was adsorbed for 10 min at $E = 0.1 \text{ V}$ vs. RHE and then removed from the electrolyte by Ar purging for 50 min keeping the electrode at the same potential. The Cu_{UPD} determination of the Pd surface area (S_{Pd}) was performed as described in Ref. [15]. The catalytic activity for the HCOOH electrooxidation was studied in the still 0.5 M HCOOH + 0.1 M H₂SO₄ electrolyte under potentiostatic and potentiodynamic regimes.

All solutions were prepared using Milli-Q purified water (18.2 MΩ cm) (Milli Pore, USA). Extra pure H₂SO₄ (Acros, 96%), HCOOH (Sigma–Aldrich, >98%, puriss. p.a., [CH₃COOH] <0.005%) and CuSO₄·5H₂O (Aldrich, 99.999%) were used for the preparation of electrolytes. Prior to each experiment, the glassware was cleaned by soaking in a H₂SO₄:H₂O₂ (1:1 v/v) mixture and then thoroughly washed with Milli-Q water.

3. Results and discussion

3.1. Characterization of catalysts

Properties of the 5 wt.% Pd/C and 5 wt.% PdC_{0.14}/C catalysts under study were analogous to those of the samples, which were prepared using the similar methods and characterized meticulously in our previous work [15]. Therefore, the characteristics of the studied catalysts are discussed here briefly, and the reader can be referred to the above-mentioned paper for more details. The XRD analysis of the synthesized catalysts (Fig. 1a) justifies that the untreated Pd/C sample contains pure palladium crystallites with the size of ca. 11 nm and the *fcc* lattice constant of $a = 3.893 \text{ Å}$, which are converted to the PdC_{0.14} phase ($a = 3.992 \text{ Å}$) with the same size of crystallites upon heating in a C₂H₄ flow at 300 °C. As evidenced by TEM (see Fig. 1b as an example for the Pd/C sample), heating the Pd/C catalyst in the presence of ethylene does not provoke a substantial increase in the mean sizes of the palladium-containing crystallites. The d_l values for the Pd/C and PdC_{0.14}/C catalysts were determined to be 6.1 ± 4.3 and $7.8 \pm 4.2 \text{ nm}$, respectively.

Typical cyclic voltammetry (CV) and CO-stripping curves measured with the catalysts under study in 0.1 M H₂SO₄ are exemplified in Fig. 2. The hydrogen underpotential deposition (H_{UPD}) region of the CV curve registered for the untreated Pd/C catalyst exhibits well-known features of pure palladium [20]. Upon treatment with ethylene, the intensity of H_{UPD} (coupled to the sulfate–bisulfate adsorption) peaks along with the signals associated with oxidation/reduction of the surface of Pd-containing particles is partially suppressed. Obviously, this suppression is caused by the formation of the amorphous carbon deposits on the surface of the particles as a result of the ethylene decomposition [15]. Generally, the transformation of the palladium nanoparticles to the PdC_{0.14} phase induces marginal changes in the modes of the H_{UPD}, CO-stripping (Fig. 2) and Cu_{UPD} (not shown) processes occurring thereon, as well as on the red-ox behavior of the surface of these particles. The specific S_{Pd} values for the Pd/C and PdC_{0.14}/C catalysts amount to 3.0 and 2.3 $\text{m}^2 \text{ g}^{-1}$ (cat.), respectively, as determined by Cu_{UPD} and CO-stripping measurements.

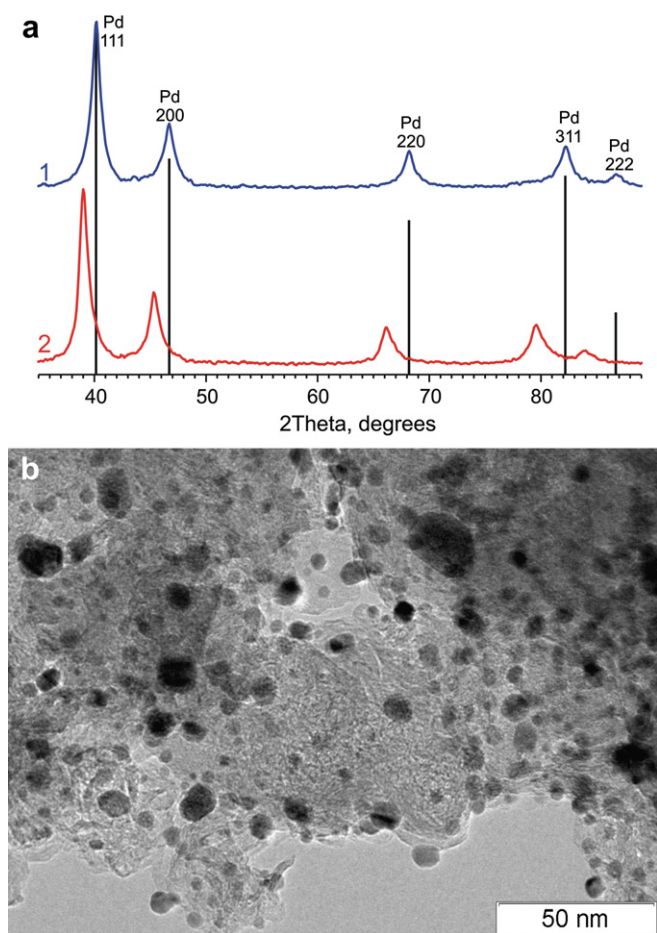


Fig. 1. (a) Background-subtracted XRD patterns of the (1) Pd/C and (2) PdC_{0.14}/C catalysts. (b) Fragment of TEM image of the Pd/C catalyst.

3.2. Catalytic activity for the HCOOH electrooxidation

Fig. 3 demonstrates the evolution of the curves of potentiodynamic HCOOH electrooxidation over the Pd/C and PdC_{0.14}/C catalysts registered by cycling the potential of the electrode in the

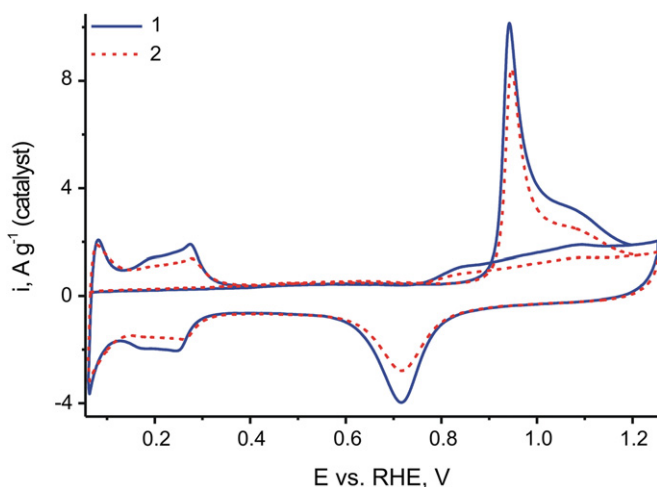


Fig. 2. CV and CO-stripping curves registered with the (1) Pd/C and (2) PdC_{0.14}/C catalysts in 0.1 M H₂SO₄ at the sweep rate of 50 mV s⁻¹ at 25 °C. Currents are normalized to the catalyst mass.

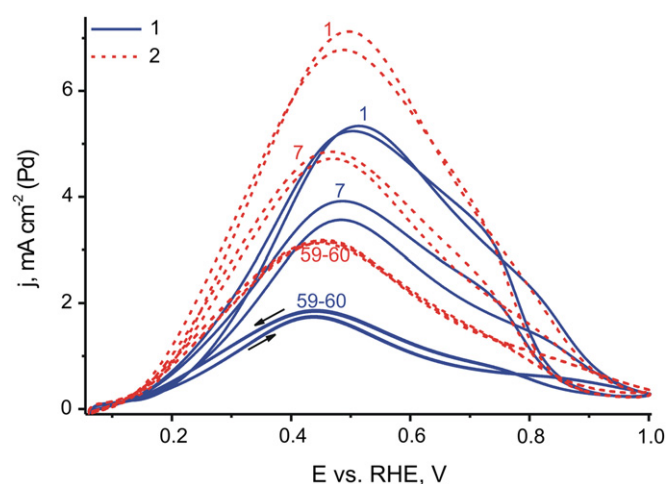


Fig. 3. Potentiodynamic oxidation of formic acid (numbers on the plot indicate the 1st, 7th, 59th and 60th scans) over the (1) Pd/C and (2) PdC_{0.14}/C catalysts in 0.5 M HCOOH + 0.1 M H₂SO₄ at the sweep rate of 50 mV s⁻¹ at 25 °C. Currents are normalized to the Pd surface area determined by Cu_{UPD} for the fresh catalysts.

0.06–1.0 V range. Juxtaposition of the CV curves presented on Fig. 3 definitely indicates that the specific catalytic activity for the HCOOH electrooxidation of the palladium carbide phase is superior to that of the palladium metal. The qualitative resemblance of the shapes of the HCOOH oxidation curves registered with the Pd/C and PdC_{0.14}/C catalysts suggests that the mechanism of the reaction is similar for both catalytic materials. During the initial period of tests, the currents associated with the oxidation of formic acid over both catalysts decrease notably, while the rate of degradation of the activity becomes appreciably slower after registration of ca. 20–30 cycles. Nevertheless, even after measuring 60–80 cycles under employed conditions, the registered HCOOH oxidation current densities over both Pd/C and PdC_{0.14}/C catalysts still diminish. This slow degradation of the activity might be partially attributed to the dissolution of palladium which may occur at high anodic potentials in acidic electrolytes [21]. Besides, it should be taken into account that numerous registration of CVs over Pd-based catalysts in the unstirred 0.5 M HCOOH solution results in notable depletion of the near-electrode layer with formic acid and, possibly, enrichment thereof with poisoning species. Thus, for more accurate tests of the long-term activity of the catalysts, potentiostatic measurements were performed. The employed low loadings of Pd on the electrode surface assured that registered currents are at least by one order of magnitude lower than those predicted for the purely diffusion-controlled process at a given concentration of HCOOH.

Potentiostatic oxidation of formic acid over the catalysts under consideration was studied at $E = 0.2$ and 0.3 V before and after registration of 70 CV curves in the potential range of 0.06–1.0 V in the same electrolyte, which was stirred before each measurement (Fig. 4). The data presented in Fig. 4 again demonstrate superiority of the non-stoichiometric palladium carbide as a catalyst for the formic acid electrooxidation over pure palladium metal. It should be noted, however, that during the initial period of the potentiostatic tests, the rate of decrease of the HCOOH oxidation current densities measured over the PdC_{0.14}/C catalyst is notably higher than that over the Pd/C sample. After 30 min of measurements at both 0.2 and 0.3 V (performed before the registration of CVs, i.e. curves 1a and 2a on Fig. 4), the specific activities of the studied catalysts are fairly close to each other with a minor (ca. 10%) advantage of the palladium carbide. When assuming the suggested above identity of the reaction mechanisms over the Pd/C and PdC_{0.14}/C catalysts, one might speculate that the transformation of

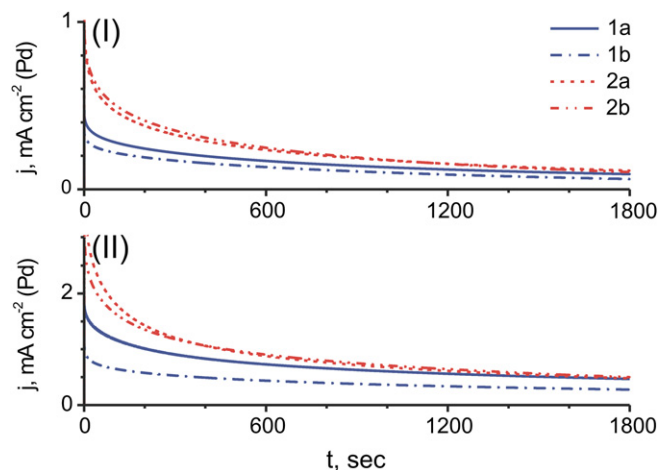


Fig. 4. HCOOH oxidation transients registered with the (1) Pd/C and (2) PdC_{0.14}/C catalysts in 0.5 M HCOOH + 0.1 M H₂SO₄ at (I) $E = 0.2$ V and (II) $E = 0.3$ V vs. RHE before (1a and 2a) and after (1b and 2b) potentiodynamic oxidation of formic acid over these electrodes during 70 scans at 50 mV s⁻¹ in the potential interval of 0.06–1.0 V vs. RHE. Currents are normalized to the Pd surface area determined by Cu_{UPD} for the fresh catalysts.

palladium to the non-stoichiometric palladium carbide increases the rates of ‘direct’ and ‘indirect’ routes of the HCOOH oxidation practically to the same extent. Thus, the rate of production of poisoning species through the ‘indirect’ route in the presence of the PdC_{0.14}/C catalyst should be notably higher than that over the Pd/C sample. Arguably, the PdC_{0.14}/C catalyst suffers stronger poisoning just due to the much higher concentration of this poison accumulated under potentiostatic conditions as compared to the unmodified Pd/C sample.

When comparing the transients of the HCOOH oxidation after the registration of 70 CVs, it is clearly seen that numerous excursions of the potential to 1.0 V provoke a drastic degradation of the specific activity of the Pd/C sample (cf. curves 1a and 1b on Fig. 4). Contrariwise, the transients registered with the PdC_{0.14}/C catalyst before and after the analogous potentiodynamic test exhibit almost identical HCOOH oxidation current densities (cf. curves 2a and 2b on Fig. 4). The CV curves measured with the catalysts under study in the supporting HCOOH-free electrolyte after performing the catalytic tests (not shown) confirmed that the observed decrease in the activity of the Pd/C sample is the consequence of the palladium dissolution. Indeed, the S_{Pd} value measured for the Pd/C catalyst after the catalytic performance tests described above amounted to ca. 65% of the initial value. At the same time, the PdC_{0.14}/C catalyst demonstrated less than ca. 10% loss of the S_{Pd} value. Normalization of the curves 1b and 2b (Fig. 4) to the final S_{Pd} would result in current densities fairly close to those exhibited by the curves 1a and 2a (Fig. 4) normalized to the initial S_{Pd} , respectively. However, this is obviously not the case for the potentiodynamic tests of the both Pd/C and PdC_{0.14}/C catalysts (Fig. 3). The latter observation suggests that, apart from the decrease in the S_{Pd} values, the registered continuous degradation of the HCOOH oxidation currents during measurement of numerous CVs (Fig. 3) is substantially caused by the changes in the composition of the unstirred electrolyte in the near-electrode layer mentioned above.

The reason for higher stability of the non-stoichiometric palladium carbide towards the dissolution at high anodic potentials is not fully understood for the moment. Probably, it might be trivially connected with the fact that amorphous carbon deposits, formed over the Pd nanoparticles during heating in a C₂H₄ flow, cover the defective sites with high affinity to oxidation at high anodic potentials on the surface of these nanoparticles and thus secure palladium from dissolution.

4. Conclusion

Non-stoichiometric palladium carbide nanoparticles were synthesized by decomposition of ethylene over the Pd/C precursor and their catalytic properties were tested for electrooxidation of formic acid. The synthesized PdC_{0.14}/C catalyst exhibits superior catalytic performance and stability during the HCOOH oxidation as compared with the unmodified Pd/C sample as demonstrated by potentiodynamic and potentiostatic studies performed at 25 °C in the 0.5 M HCOOH + 0.1 M H₂SO₄ solution. The improved catalytic activity of non-stoichiometric palladium carbide is suggested to be a consequence of the modification of electronic properties of Pd under the action of interstitial carbon atoms [16]. Modification of the electronic properties of palladium due to its combination with other metals and consequent sound changes in the catalytic performance of Pd for the HCOOH electrooxidation were described earlier, particularly, in the seminal paper by Kibler et al. [11]. Juxtaposition of the electrochemical and electrocatalytic properties of carbon-modified Pd observed here (and earlier in Ref. [15]) with those reported in Ref. [11] for Pd/M(111) structures demonstrates that the nature of the promoting effect of interstitial carbon and metal substrates differ to a great extent. Indeed, the latter produce both changes in the value of the current maximum of the HCOOH electrooxidation and shift of the HCOOH electrooxidation peak in the CV tests (e.g., the Pt(111) substrate produces ca. 0.2 V shift of the peak maxima to lower potentials [11]), while the carbon-promoter boosts the catalytic activity of Pd keeping the potentiodynamic profile of the HCOOH electrooxidation qualitatively immutable (Fig. 3).

The samples with comparatively low Pd loading were employed in the present work as model catalysts for the sake of demonstration of the promoting action of the interstitial carbon on the catalytic performance of palladium nanoparticles in the electrooxidation of formic acid. However, as demonstrated before [22], the employed synthetic protocol (slightly modified) can be effectively applied for the preparation of the Pd/C catalysts for fuel cells with much higher loading. Since the PdC_x catalysts can be easily fabricated from any Pd/C precursor by simple heat-treatment in an ethylene or other unsaturated hydrocarbons flow (or even in a H₂ flow in the case of high degree of disorder in a carbon support [15]), carbon-supported nanoparticles of the palladium-carbon interstitial solid solutions should be considered as a promising materials for the practical applications as anode catalysts for DFAFCs.

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